# HYDROGEN FUTURES AND TECHNOLOGIES

Dr. Charles W. Forsberg

Oak Ridge National Laboratory<sup>\*</sup> P.O. Box 2008 Oak Ridge, Tennessee 37831-6179 Tel: (865) 574-6783 Fax: (865) 574-9512 Email: <u>forsbergcw@ornl.gov</u>

Prepared for Rohsenow Symposium on Future Trends in Heat Transfer Massachusetts Institute of Technology Cambridge, Massachusetts Friday, May 17, 2003

> Panel on Heat Transfer in Energy Manuscript Date: April 15, 2003 File Name: Hydrogen: MIT.2003

The submitted manuscript has been authored by a contractor of the U.S. Government under contract DE-AC05-00OR22725. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

<sup>&</sup>lt;sup>\*</sup>Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725.

# HYDROGEN FUTURES AND TECHNOLOGIES

#### **Charles W. Forsberg**

#### Abstract

Concerns about the security of oil supplies and the environmental consequences of burning fossil fuels have transformed the idea of a hydrogen ( $H_2$ ) economy from science fiction into a political bipartisan vision of our energy future. The challenge is now one of economics and technology. In one context, we already have a rapidly growing  $H_2$  economy, driven by the need for increased supplies of  $H_2$  to convert more abundant lower-grade crude oils into clean liquid fuels. This development is creating the infrastructure for a global  $H_2$  economy and provides powerful incentives to develop better methods of  $H_2$ production. The  $H_2$  content of liquid fuels is a variable; thus, there is also the option to add additional  $H_2$ to conventional liquid fuels to create  $H_2$ -enhanced fuels. This option increases the liquid fuel yield per barrel of oil, creates a greatly expanded  $H_2$  production infrastructure, and may provide the easiest transition to a full  $H_2$  economy.

It is primarily the characteristics of  $H_2$  as a fuel, rather than the type of device in which it is used (fuel cell or internal combustion engine), that creates the environmental benefits of a  $H_2$ -fueled economy at the point at which the device is used. Water is the only waste product of  $H_2$  fuel. The other potential benefits of a  $H_2$  economy require methods of production that do not depend upon foreign energy resources and greatly reduce emission of greenhouse gases to the environment. Consequently, the most important challenges are the development of better methods to produce  $H_2$  and to store (deliver)  $H_2$  onboard vehicles. While fuel cells are not required for a revolution in transportation (internal combustion engines can burn  $H_2$ ), they add another dimension to the  $H_2$  economy by their potential impacts on electricity production and distribution. Hydrogen fuel cells may provide a storable form of electricity to meet peak electric demands. This benefits high-capital-cost low-production-cost energy sources such as nuclear and renewables by providing a demand for their energy output that is not tied to the daily cycle of electricity demand.

The methods to produce and store  $H_2$  define the technical challenges. These challenges, in turn, define the challenges in heat transfer—the subject of this Rohsenow Symposium. The likely characteristics of our transition to a  $H_2$  economy and some of the accompanying technical challenges in heat transfer are described herein.

#### 1. Introduction

The hydrogen  $(H_2)$  economy has become the organizing construct when energy futures are considered. An  $H_2$  economy is a potential solution for two critical issues: (1) providing reasonably priced transport fuels that are not dependent on foreign suppliers and (2) reducing the environmental degradation from vehicle air pollution—including greenhouse gas emissions. While national security concerns drive energy policies in the United States, those in Europe are driven by environmental concerns. The differences in emphasis for development of a  $H_2$  economy reflect underlying economic and historical factors. Europe has historically imported liquid fuels. To reduce the risks of energy shortages and encourage efficient use of fuels, European fuels are heavily taxed. The United States has historically been an exporter of energy and has built its transport and industrial infrastructure on low-cost energy. Although the United States has become a massive importer of liquid fuels, it has not yet restructured its economy for this more expensive source of energy. If the cost of oil doubles, European fuel prices are increased by 25%, but those in the United States are doubled. For a country with a low-cost-energy infrastructure, the cost of oil determines the health of the economy. The environmental emphasis of Europe reflects the lower economic impacts of a rise in energy prices and a longer history of pollution associated with high population densities.

Pure  $H_2$ , like electricity, is an energy carrier. Because  $H_2$  does not exist on earth in significant quantities, it must be manufactured. Any energy source can be used to manufacture  $H_2$ , including fossil, nuclear, and renewable energy sources. This is a major advantage because different parts of the world have different primary energy sources. When burned,  $H_2$  yields only water and thus is the ultimate clean fuel. The manufacturing processes for  $H_2$  production generate various types of pollutants; however, it is significantly easier to control the pollution from a few thousand facilities than from hundreds of millions of vehicles. Last, the potential exists for efficient low-cost conversion of  $H_2$  to electricity with fuel cells and electricity to  $H_2$  with electrolysis. Efficient interconvertibility would allow  $H_2$  to be a stored form of electricity and permit lower-cost nighttime electricity to be used for  $H_2$  production.

While the advantages of a  $H_2$  economy are self-evident, the technical challenges that must be overcome to create an economically viable  $H_2$  economy are significant. The success in this endeavor will determine the timing and scope of the  $H_2$  economy. This paper provides a perspective on hydrogen futures, the technical challenges involved, and some examples of issues in heat transfer that must be addressed to meet the technical challenges.

#### 2. Hydrogen Futures

Large-scale  $H_2$  production and use is an old business. Starting in the mid 1800s, major cities installed town-gas systems for lighting and heating in businesses and homes. Town gas is produced by mixing water and hot coal to produce a gas that is typically 50%  $H_2$ , with the remainder being carbon monoxide and carbon dioxide. Town gas was ultimately replaced by natural gas, with the last major town-gas systems shutting down in the 1970s.

Today, worldwide  $H_2$  consumption is - 50 million tons/year with expected future  $H_2$  growth rates of 4 to 10%. The primary applications are the production of fertilizer and the upgrading of heavy crude oil to gasoline. World-class  $H_2$  plants have production capacities of 200 million standard cubic feet of  $H_2$  per day (scf/d). New plants have been announced with capacities of 300 million scf/d [1200 MW(t) of  $H_2$  energy, based on the higher heating value]. The next-generation ammonia plants (large  $H_2$  consumers) are expected to produce 3000 tons/day of ammonia, requiring 200 million scf/d of  $H_2$ . Most of these plants use steam reforming of natural gas to produce  $H_2$ . Supporting this production system are major pipelines, underground bulk storage caverns for  $H_2$ , and a variety of other specialized facilities.

The world is exhausting its supplies of light crude oil, which requires little processing to produce liquid fuels. The near-term growth market for  $H_2$  is the upgrading of the more abundant low-cost heavy crude oils and tar sands to clean gasoline and diesel fuels. These crude oils have  $H_2$ -to-carbon ratios as low as 0.8. The  $H_2$ -to-carbon content of the crude oil components must be raised to - 1.5 to produce usable liquid fuels.

The characteristics of the world oil-based economy create a near-term  $H_2$ -economy option: the use of  $H_2$ enhanced fuels (Uhrig 2003). The adoption of  $H_2$ -enhanced fuels would create much of the infrastructure (production plants, pipelines, and storage facilities) required for a transition to a full-scale  $H_2$  economy. The ratio of  $H_2$  to carbon in liquid fuels is a variable. If low-cost  $H_2$  were available, the energy yield of gasoline, jet, and diesel fuel per ton of oil could be increased by up to 15% by increasing the  $H_2$ -to-carbon ratio in the final product. This increase is accomplished partly by breaking one ring of the double- and triple-ring compounds in liquid fuels and saturating the carbon chain with  $H_2$ .

The H<sub>2</sub>-to-carbon ratio is dictated by economics. The economics are near breakeven. If the price of oil is increased or the price of H<sub>2</sub> is decreased, further hydrogenation of fuel would be adopted. However, there is a problem with this approach. Most H<sub>2</sub> is made from natural gas. Natural gas and crude oil prices are coupled because (1) both can be used as boiler fuel and (2) natural gas can be converted to liquid fuels. As a consequence, if oil prices rise, natural gas and H<sub>2</sub> prices would also rise. If economic H<sub>2</sub> from other energy sources can be developed, (1) the links between oil, gas, and H<sub>2</sub> prices would be broken and (2) more H<sub>2</sub> could be added to the liquid fuels as oil prices rise.

Other benefits arise from additional hydrogenation of liquid fuels. With the production of more fuel per ton of oil, the  $CO_2$  emissions from the burning of liquid fuels are decreased. The sulfur content of liquid fuels is also reduced because the processes that add H<sub>2</sub> to liquid fuels remove sulfur as well. Smaller quantities of nitrogen oxides are formed in internal combustion engines (ICEs) because H<sub>2</sub>-rich fuels lower the peak burn temperature in the combustion chamber. The particulate emissions from diesel engines are also reduced, because the H<sub>2</sub> addition reduces the quantities of multiring carbon compounds in diesel fuel—the compounds primarily responsible for soot from diesel engines.

Oil companies in Europe are studying H<sub>2</sub>-enhanced fuels as part of a strategy to limit greenhouse gases from liquid fuels. In Norway, a large-scale CO<sub>2</sub> sequestration demonstration is being conducted on an offshore platform. Natural gas with a high CO<sub>2</sub> content is extracted. The CO<sub>2</sub> in the natural gas is separated and then sequestered by injection into deep geological strata. In such a system, the natural gas could be converted to H<sub>2</sub> using steam reforming with sequestration of this additional CO<sub>2</sub>. This creates a CO<sub>2</sub>-free H<sub>2</sub> for use in H<sub>2</sub>-enhanced liquid fuels.

In the longer term, some type of  $H_2$ -fueled transportation system is likely; however, this system could take several forms. Although the public generally assumes that a  $H_2$ -fueled transportation system implies cars with fuel cells, ICEs can be designed to operate well on  $H_2$ . Ford (Natkin 2003) has demonstrated  $H_2$ -fueled ICEs with up to 25% better efficiency than an equivalent gasoline ICE. Equally noteworthy, only minor modifications of existing engines were required. In hybrid vehicles, the  $H_2$ -fueled ICE has up to 50% better fuel economy than the equivalent gasoline-fueled vehicle. Hydrogen-fueled ICEs are capable of meeting "zero-emission" goals for vehicles. Hydrogen fuels avoid the generation of greenhouse gases, hydrocarbon, and carbon monoxide pollutants. Without the hydrocarbon and carbon monoxide pollutants, very-efficient control of the other vehicle pollutant, NO<sub>x</sub>, is relatively simple. Dual-fuel vehicles that burn gasoline and  $H_2$  are also possible: such options reduce fuel transition issues. The costs of a  $H_2$ -fueled ICE is about the same as that for today's gasoline-powered engines and could be manufactured using existing facilities on a relatively short time scale.

The major advantage of  $H_2$  fuel cells compared with ICEs is that the efficiency is expected to be double that of an equivalent-powered gasoline ICE. The cost of fuel cells must be reduced by a factor of 10 to be competitive for automotive applications. However, fuel cells are becoming competitive for certain specialized industrial markets, which should aid the commercialization of this technology. Although it is likely that fuel-cell goals for automotive vehicles will ultimately be met, ICEs may be the transition power plant for decades. The initial large market for fuel cells may be electricity generation, a market that does not require such severe reductions in fuel cell costs to become viable. The cost of electricity follows demand and varies widely over the period of a day. The high-efficiency conversion of  $H_2$  to electricity with fuel cells may make  $H_2$  viable as a form of electricity storage to better match production with demand. If this can be achieved, it has enormous implications. It would create a massive demand for  $H_2$  and result in the development of a large  $H_2$  infrastructure. This would benefit high-capital-cost, low-operating-cost energy sources (nuclear and renewable energy sources) by providing a market for energy to produce  $H_2$  in periods of low electricity demand. Furthermore, large pipelines carry a factor of ten more energy than large transmission lines, thus providing a method to bypass the bottlenecks in the electrical transmission grid that occur during periods of high electricity demand. Last, some types of fuel cells reject heat at medium to high temperatures. This characteristic, combined with the low pollution potential, may finally make viable the co-generation of electricity and heat on a small scale.

#### 3. Technical Barriers to a H<sub>2</sub> Economy

The major incentives to develop a  $H_2$  economy are energy security and a cleaner environment. These goals define the most important technical barriers that need to be overcome:

- *Low-cost carbon-free* H<sub>2</sub> *production*. From a global perspective, low-cost carbon-free H<sub>2</sub> production probably implies nuclear-generated H<sub>2</sub> or steam reforming of fossil fuels with CO<sub>2</sub> sequestration. The challenges are greater for renewables production of H<sub>2</sub> because of conflicting land use issues and the economics of scale. The efficiency and cost of hydrogen compression, purification, and storage operations are more sensitive to the scale of operations than comparable activities with electricity.
- *Vehicle onboard* H<sub>2</sub> *storage*. While most of the prototype H<sub>2</sub> vehicles store H<sub>2</sub> in high-pressure carbon-fiber cylinders, there are also various solid storage media. All of these options have serious limitations such as excessive weight, large volumes, or complicated refueling schemes. Such systems are probably workable for some types of fleet operations, such as municipal buses, and may evolve into practical systems for cars. However, the jury is still out. If H<sub>2</sub> is to be used for vehicles, H<sub>2</sub> vehicle storage issues must be resolved.

In terms of meeting the goals of a  $H_2$  economy (secure reasonably priced energy resources and ensure low environmental impacts), the fuel cell would be highly desirable. However, it is not a requirement. The primary benefit of using fuel cells in transportation is to reduce the requirements to lower the cost of manufacturing  $H_2$ . A more efficient fuel cell can use higher-cost  $H_2$  for the same cost per mile of operating a vehicle. The initial impact of fuel cells may be on electric generation where the cost and weight constraints are less.

## 4. Heat Transfer Challenges

Today's symposium is to address challenges in heat transfer. Having defined the critical technical challenges to a  $H_2$  economy, I would like to give two examples of circumstances in which heat transfer issues are a significant part of the challenge. These examples represent opposite extremes of heat transfer research.

#### 4.1 Generation of Hydrogen Using Nuclear Energy

The leading technologies for the production of  $H_2$  using nuclear energy are thermochemical cycles in which water and high-temperature heat are input into a series of chemical reactions that yield  $H_2$  and oxygen. Except for the water, all of the other chemicals within these cycles are fully recycled. Over 100 such cycles have been identified. The estimated thermal-to- $H_2$  efficiency for the best of these processes is >50%. The Japanese investigators estimate [OECD-NEA 2000] that the cost of nuclear thermochemical  $H_2$  production may be as low as 60% of that for  $H_2$  production by the electrolysis of water. The projected cost is lower than that for electrolysis because a thermochemical process converts heat directly to  $H_2$  whereas electrolysis involves conversion of heat to electricity and the electricity to  $H_2$ . Added conversion steps increase inefficiencies and capital costs. The leading candidate is the sulfur–iodine process which consists of three chemical reactions:

$2H_2SO_4 Y 2SO_2 + 2H_2O + O_2$	(Heat input at 750 to 950EC)
2HI Y I <sub>2</sub> + H <sub>2</sub>	(Heat input at 450EC)
$I_2 + SO_2 + 2H_2OY 2HI + H_2SO_4$	(Heat rejection at 120EC)

These processes were initially examined in the 1970s. Significant technical challenges were identified. There is renewed interest these technologies because of (1) the market growth in near-term  $H_2$  demand [EPRI 2003] with the massive longer-term potential for a  $H_2$  economy and (2) advances in separations technologies in Japan [Onuki 2003] and the United States that may significantly improve the economics and process viability. All of these cycles impose similar requirements on the nuclear reactor: deliver large quantities of high-temperature heat [2400 MW(t) to match the capacity of plants under construction that will produce  $H_2$  from natural gas] from the reactor to the  $H_2$  production plant. A schematic of the system is shown in Fig. 1. This type of system presents several challenges in heat transfer:

- Intermediate heat transfer system. Heat must be transferred efficiently over significant distances between the reactor and the H<sub>2</sub> production facility. The separation distance is required to ensure the safety of the nuclear facilities from any accidents in the chemical plants. The size [up to 2400 MW(t)], temperature (~800EC), and distance (500 to 1000 m) of this heat transfer system are substantially beyond industrial experience. A number of studies performed in Germany in the 1970s indicated that molten-salt heat-transfer fluids would be preferred. These salts have high heat capacities (typically four times that of sodium), low pumping costs, and low vapor pressures. They are unreactive with air but will slowly react with water.
- *Reactor coolant.* The reactor must provide heat to drive these systems. One of the two reactor candidates [Forsberg 2003] for this mission is the Advanced High-Temperature Reactor (AHTR) [Forsberg, Pickard, and Peterson 2003]. The AHTR uses a molten salt coolant (mixture of sodium, zirconium, and other fluoride salts) to move heat from the solid fuel in the reactor core to the thermochemical process through an intermediate heat transfer loop. Because these salts boil at about 1400EC, the reactor operates at atmospheric pressure. Heat must be delivered at high temperatures—750 to 900EC. That implies that the reactor core is operating at significantly higher temperatures. These temperatures are near practical engineering materials limits; thus, efficient heat transfer is required to reduce the reactor peak temperatures and minimize the challenging materials limitations.



Fig. 1. The advanced high-temperature reactor, heat transfer loop, and hydrogen thermochemical production facility.

In terms of engineering heat transfer, molten salt behavior at these temperatures is not fully understood. Molten salts are very-high-heat-capacity, optically or semioptically transparent, low-viscosity fluids (Fig. 2). At these operating temperatures, radiation heat transfer (which varies as the fourth power of the absolute temperature and depends upon radiation absorption properties) becomes an important mechanism of heat transfer. Traditional liquid-cooled heat-transfer correlations do not account for radiation heat transfer. Although radiation heat transfer is reasonably well understood in gas-phase systems, such systems generally have very low heat capacities. For these molten-salt systems, there are many questions. How should one design such a system for maximum efficiency? Should surfaces be treated to enhance radiation heat transfer? What are the optimum optical properties of the molten salt to maximize heat transfer? Are there incentives to modify the optical properties of the coolant? This is an area of heat transfer in which little work has been done.

## 4.2 Hydrogen Storage and Fuel Cells

At the opposite extreme are the heat transfer challenges for  $H_2$  storage devices and fuel cells. These devices are small chemical reactors that operate at low temperatures and where reasonably precise control of temperature is required because chemical kinetics is strongly dependent upon the temperature. The challenges here are primarily economic. For vehicle applications, the systems must be small, low cost, efficient, and have rapid-start capabilities.



Fig. 2. Transfer of molten salt in air.

The ideal  $H_2$  storage media would be a solid that stores  $H_2$  at low pressure and releases the  $H_2$  upon heating. Many types of such media are being investigated: metal hydrides, carbon forms, etc. The ideal system would efficiently heat a small fraction of the total storage media, release its  $H_2$ , and then cascade the heat efficiently to preheat the next fraction of the storage media to release its  $H_2$ . Such a process would maximize thermal efficiency, minimize startup times, and enhance safety by having only a small inventory of  $H_2$  gas. After the  $H_2$  is released from a section of the media, that section must be isolated from the rest of the storage media so that it does not absorb  $H_2$  upon cooldown. While it is easy to conceive of a system with complex valves and various heat transfer fluids that accomplishes these tasks, the development of a simple, reliable, economic heat-management system is a serious challenge.

For automobile fuel cells, heat management requires maintaining constant temperature in a compact device with low energy costs and small low-cost auxiliary systems. Because the waste product from a fuel cell is water, the need also exists to control water balances so that the fuel cell does not dry out or become flooded.

#### 5. Conclusions

Today, at the Rohsenow Symposium on Future Trends in Heat Transfer, we are discussing the frontiers of heat transfer. The  $H_2$  economy is the organizing concept for one energy frontier. As such, it presents a wide variety of challenges in heat transfer. However, unlike space or military applications, strong economic constraints are associated with the production and use of  $H_2$ . Energy is one of our largest economic sectors, which creates very large incentives to improve performance at low costs. The viability of a  $H_2$  economy strongly depends upon technical advances including those in heat transfer.

#### 6. References

Electric Power Research Institute, 2003. *High-Temperature Gas-Cooled Reactors for the Production of Hydrogen: An Assessment in Support of the Hydrogen Economy*, Report No. 1007802, Palo Alto, California.

Forsberg, C. W., Paul S. Pickard, and Per F. Peterson, 2003, "Molten-Salt-Cooled Advanced High-Temperature Reactor for Production of Hydrogen and Electricity," *Nuclear Technology*, (in press).

Forsberg, C. W., 2003. *"Hydrogen Production Process Requirements and Nuclear Reactor Options," Proc. 2<sup>nd</sup> Topical Conference on Fuel Cell Technology* (Embedded Topical Conference within the 2003 Spring American Institute of Chemical Engineers Annual Meeting, New Orleans, Louisiana, March 31–April 3, 2003), American Institute of Chemical Engineers, New York.

Natkin, R. J., X. Tang, B. Boyer, B. Oltmans, A. Denlinger, and J. W. Heffel, 2003, "Hydrogen IC Engine, Boosting Performance, and NO<sub>x</sub> Study," 2003. *SAE Technical Paper 2003-01-0631, Proc. 2003 SAE World Congress, Detroit, Michigan, March 3–6, 2003*, SAE International, Warrendale Pennsylvania.

OECD-NEA Nuclear Science Committee, 2000, Proc. First International Exchange Meeting on Nuclear Production of Hydrogen, Paris, France, October 2–3, 2000.

Onuki, K. et al., 2003, "*R&D on Iodine-Sulfur Thermochemical Water Splitting Cycle at JAERI*," *Proc.* 2<sup>nd</sup> *Topical Conference on Fuel Cell Technology* (Embedded Topical Conference within the 2003 Spring American Institute of Chemical Engineers Annual Meeting, New Orleans, Louisiana, March 31–April 3, 2003), American Institute of Chemical Engineers, New York.

R. E. Uhrig, 2003. "Hydrogen Enhanced Hydrocarbon Transportation Fuels," Statement of Interest for the DOE Climate, Mechanical Engineering Magazine Online, **www.memagazine.org/contents.current.webonly/webex324.htm**.